Madelung Potentials and Disorder Broadening of Core Photoemission Spectra in Random Alloys

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We present the first experimental evidence for "disorder broadening" of core level x-ray photoemission line shapes in alloys. The broadening is attributed to variations in electrostatic potential. A model in which the charge on a site is assumed to be proportional to its number of unlike neighbors has recently been shown to greatly improve the calculated total energies of disordered alloys. This model predicts a broadening a factor of 2 larger than observed. We discuss this result in terms of short range order and a generalized charge model. [S0031-9007(97)03188-8]

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Since the work of Madelung [1] the electrostatic energy of arrays of charges has attracted continued attention [2]. However, although the concepts of electronegativity and ionicity have had great historical importance in chemistry, solid state physicists are reluctant to consider "charge transfer" as this does not constitute a quantum mechanical observable and the concept is therefore vague and arbitrary. In recent years the inclusion of Madelung energies for disordered systems, previously assumed to be zero, has been shown to be essential to a truly *ab initio* description of the physical and electronic structure of random alloys [3,4], forcing a reexamination of the charge transfer picture. In particular, a model in which the charge on a site is determined by the *local* composition has gained increasing support [3–5] and has been used [6] to explain the structural stability of a wide range of compounds and alloys.

In this Letter we present the first experimental study of the Madelung *potential* in random alloys. One expects that variation in local bonding configuration will give a distribution of potentials, but no such "disorder broadening" has previously been observed with core level x-ray photoelectron spectroscopy (XPS). We estimate the magnitude of disorder effects and present high resolution experimental data showing the first observation of disorder broadening in the core level XPS of random alloys. This comparison of theory and experiment goes to the heart of our understanding of the electronic structure and bonding in alloys, giving insight into local charge neutrality, short range order, and charge correlation.

The electrostatic potential at lattice point i in a random alloy relative to the corresponding elemental solid can be expressed as a sum of intra-atomic and Madelung potentials,

$$V^i = \frac{14.4}{R}\left\{2Q^i + \sum_{m=1}^{\infty}\frac{1}{\rho_m}\sum_{j\in m}Q^j\right\}. \tag{1}$$

If Q is measured in units of e, the electronic charge, and the nearest neighbor distance R is in Å, then the potential is in volts. (We suppress the 14.4 factor in subsequent equations for brevity.) The first summation in the Madelung term is over concentric spheres with radius $R\rho_m$ centered on site i, and the second is over the Z_m sites in the mth shell. To characterize the distribution of potentials we first require a model for the charges Q^i at each site.

One may suppose that the Q^i are determined by c^i, the composition fraction for the species type at that site. For a random binary alloy A_xB_{1-x} charge neutrality requires

$$-Q^A c^A = Q^B c^B, \tag{2}$$

where $c^A = x$ and $c^B = 1 - x$. We refer to this as the fixed charge model (FCM) since the charges do not vary with local environment but merely reflect global stoichiometry. Although Madelung effects vanish on average within the FCM, the potential at any given site may be considerable. The average potential for a site with a particular number of "unlike" nearest neighbors N_u is

$$\langle V^i(N_u)\rangle_{i=A(B)} = \frac{Q^{A(B)}}{R}\left\{2 + Z_1 - \frac{N_u}{1 - c^{A(B)}}\right\}. \tag{3}$$

Assuming $|Q^{A(B)}| \sim 0.1$, Eq. (3) predicts an average change of approximately 1 eV in potential per unit change in N_u. This would imply considerable disorder broadening of core level XPS spectra in random alloys, an expectation contradicted by experiment. Likewise *ab initio* electronic structure calculations based on the coherent potential approximation (CPA) which implicitly use the FCM fail to predict structural properties of alloys [3,4]. We conclude that the FCM does not give a useful description of charges in disordered alloys.

Chemical wisdom suggests that an atom surrounded by all "like" atoms will be approximately neutral while an atom bonded to all "unlike" atoms will experience the maximum possible charge transfer. This means that the *charges* are correlated even when the *site occupations* are truly random [5]. Magri *et al.* have suggested [5] a correlated charge model (CCM) with the form

$$Q^i = \lambda\sum_{j\in nn^i}(S^i - S^j) = 2\lambda N_u S^i, \tag{4}$$

where nn^i denotes the nearest neighbors of site i, λ determines the ionicity, and $S^{A(B)} = -1(+1)$. Johnson and

Pinski [4] have recently developed the "charge-correlated CPA" in which the charge on site i is assumed to be determined solely by the number of unlike neighbors N_u, although no assumption of linearity is made. This "$(Z_1 + 1)$-site" theory gave a dramatic improvement in alloy formation energies, and the self-consistently determined charges for the $Z_1 + 1$ components were found to be linear in N_u and with gradient independent of composition. These results provide considerable justification for the CCM. Combining Eqs. (1) and (4) it can be shown [7] that

$$\langle V(N_u)\rangle_{A(B)} = 2\frac{\lambda}{R} S^{A(B)} Z_1\{Z_1 - 1 - \Sigma\}\{1 - c^{A(B)}\} + N_u 2\frac{\lambda}{R} S^{A(B)}\{2 - Z_1 + \Sigma\}, \qquad (5)$$

where Σ is the lattice dependent constant defined by

$$\Sigma = \sum_m \frac{K_m Z_m}{\rho_m Z_1} \qquad (6)$$

and K_m is the number of sites that are simultaneously nearest neighbors of the central site and of a site in the mth shell [3]. Eq. (5) shows that for a given lattice the average potentials are linear in N_u with gradient independent of composition. The variation of $\langle V(N_u)\rangle_A$ with N_u and its decomposition into Madelung and intratomic components are plotted in Fig. 1 for the $A_{0.5}B_{0.5}$ alloy where $R = 3$ Å and $\lambda = 0.1/Z_1$ (corresponding to an average charge of 0.1) were assumed. The Madelung part of $\langle V(N_u)\rangle_{A(B)}$ scales faster with N_u than the intratomic part but with opposite sign to $S^{A(B)}$, and so the total potential varies with $-N_u S^{A(B)}$. The gradient of $\langle V(N_u)\rangle$ against N_u is ~0.1 eV, suggesting a modest disorder broadening of alloy core level XPS spectra.

To investigate the distributions of the $V^i(N_u)$ about their averages the potentials at sites near the center of a large $A_{0.5}B_{0.5}$ cluster were calculated with the charge on each site determined according to Eq. (4) [7]. The calculated distribution for each N_u are shown in Fig. 2 and were found to be Gaussian with FWHM smaller than the gradient of $\langle V(N_u)\rangle$ against N_u (i.e., the component splitting). Thus the core potential at a site is determined predominantly by the composition of its nearest neighbor shell. Comparison with the Gaussian in Fig. 2 shows that the overall effect of disorder is an approximately Gaussian broadening with FWHM ~4 times the component splitting. Calculations for surface sites [7] revealed a slightly shallower N_u dependence, while the subsurface layer was essentially bulklike.

Considering briefly the core level binding energy shifts predicted by the CCM, we note that the center of mass of the spectra $\overline{V}$ can be obtained by averaging out the N_u dependence of $\langle V(N_u)\rangle$ in Eq. (5) to give

$$\overline{V}_{A(B)} = \frac{\overline{Q}_{A(B)}}{R} = 2\frac{\lambda}{R} S^{A(B)} Z_1\{1 - c^{A(B)}\}, \qquad (7)$$

indicating a linear dependence of the core level binding energy on composition [8]. The first equality shows that in the CCM the effective Madelung constant in disordered alloys is $\alpha^{\mathrm{eff}} = 1$ for all lattices and for all compositions. We find [7] there is on average a charge of $-\overline{Q}^A$ in the first shell, while all subsequent shells are on average charge neutral. Shells with $m > 1, K_m \neq 0$ contribute to the average Madelung energy but not the average Madelung potential $\overline{V}$. Clearly for disordered systems a distinction must be made between Madelung constant corresponding to the electrostatic *potential* and the electrostatic *energy*. For the latter quantity Magri *et al.* [5] found a parabolic variation with x.

We now use the potentials calculated for the $A_{0.5}B_{0.5}$ cluster to simulate XPS spectra using the expression

$$\langle f^i(\omega)\rangle_{A(B)} \propto \sum_{i=A(B)} L^{\Gamma}(\omega, V^i), \qquad (8)$$

where we have assumed that the component spectra $f^i(\omega)$ are given by $L^{\Gamma}(\omega, V^i)$, Lorentzians with FWHM Γ, and position determined by V^i, the potential at site i. Since

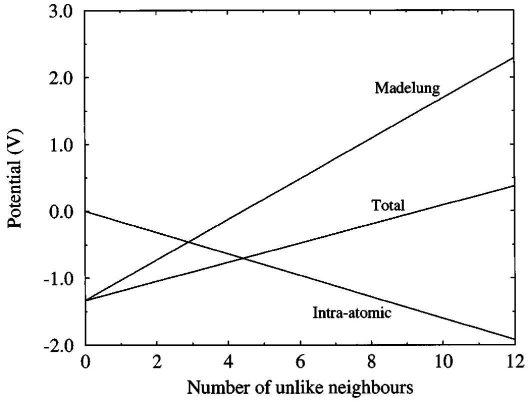

FIG. 1. The variation of $\langle V(N_u)\rangle_A$ the average potential for A sites with a given number of unlike neighbors with N_u for the $A_{0.5}B_{0.5}$ FCC lattice. The decomposition into intra-atomic and Madelung potentials is also shown.

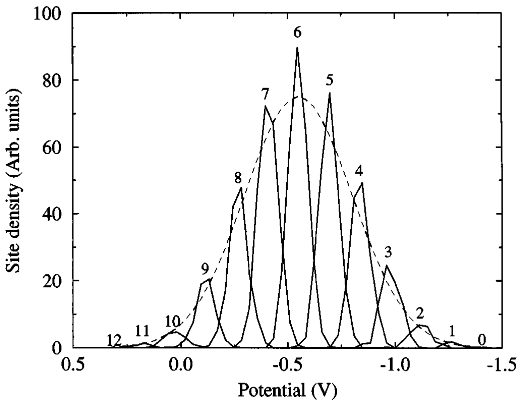

FIG. 2. The distribution of potentials for each value of N_u for an $A_{0.5}B_{0.5}$ FCC lattice. Also shown is a Gaussian distribution with FWHM given by 4.2 times the peak separation.

the V^i are determined primarily by the composition of the nearest neighbor shell it follows:

$$\langle f^i(\omega)\rangle_{A(B)} \approx \sum_{N_u=0}^{Z_1} P(N_u) L^{\Gamma}[\omega, \langle V(N_u)\rangle_{A(B)}], \tag{9}$$

where $P(N_u)$ is the probability of a site having a given N_u. We refer to this expression as the "nearest neighbor approximation" (NNA). A further approximation,

$$\langle f(\omega)\rangle_{A(B)} \approx L^{\Gamma}(\omega, \overline{V}_{A(B)}), \tag{10}$$

referred to as the average neighbor approximation (ANA) assumes a single effective $A(\underline{B})$ environment which experiences the average potential $\overline{V}$. Comparison of $\langle f^i(\omega)\rangle$ determined using Eq. (8) (the exact result) and 10 (the ANA) will determine explicitly the magnitude of disorder broadening. Further comparison of spectra calculated using Eqs. (8) and (9) will test the validity of the NNA. These comparisons are made in Fig. 3 where $\Gamma = 0.6$ eV and a Gaussian broadening of $W = 0.3$ eV FWHM were used to simulate lifetime broadening and experimental resolution, respectively. Core level XPS spectra of disordered alloys have previously been interpreted in terms of a single bulk component. Provided the chosen value of λ/R is realistic, the simulations described above show that "third generation" XPS spectrometers, which achieve $W \sim 0.25$ eV, should be capable of observing disorder broadening in alloys. Figure 3 also shows that the NNA performs extremely well.

Wolverton and Zunger have pointed out [6] that one can estimate the charge transfer parameter λ by collapsing the charge density onto the lattice sites so that the electrostatic energy of the resulting point charge array reproduces that the first principles calculations. In this way they obtained $\lambda \sim 0.006$ for CuPd alloys. Combining this value with the Cu lattice parameter we obtain $\lambda/R \sim 0.0024$. This closely corresponds to the parameters used in the preceding simulations. With this value of λ/R Eq. (7) predicts a shift in Cu $2p$ binding energy of up to 1 eV in $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloys, in broad agreement [8] with experiment [9,10]. The inverse lifetime Γ in the simulations corresponds to that of the Cu $2p_{3/2}$ level [11]. Thus our choice of parameters seems generally sound and should be particularly relevant to $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloys. An interatomic charge transfer model of photoelectron shifts is expected to work well here since intra-atomic charge redistribution is unimportant for Cu sites in $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloys [12]. Although Wolverton and Zunger [6] identified a number of more "ionic" alloy systems (CuAu, AlNi, PtNi, LiAl) the stronger electrostatic effects in these system favor the formation of intermetallic compounds rather than solid solutions. We conclude that the $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloy system provides the optimum test case for the experimental identification of disorder broadening.

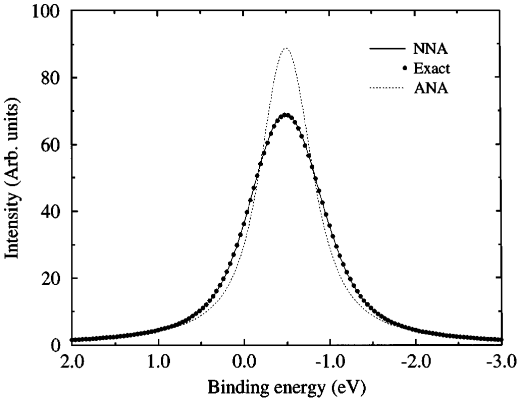

FIG. 3. Comparison of exact (circles), NNA (solid curve), and ANA (dotted curve) simulated XPS spectra for the random $A_{0.5}B_{0.5}$ FCC lattice.

Disordered polycrystalline samples of $\mathrm{Cu}_{0.5}\mathrm{Pd}_{0.5}$ and $\mathrm{Cu}_{0.8}\mathrm{Pd}_{0.2}$ were prepared by melting the requires proportions of high purity component metals under Ar in an arc furnace followed by rapid quenching. Homogeneity was ensured by repeated reorienting and remelting. Specimens were examined using the Scienta ESCA 300 spectrometer at the RUSTI facility at Daresbury Laboratory along with a pure Cu specimen. The specimen surfaces were mechanically cleaned *in situ* and photoelectron spectra were obtained at near normal emission using a monochromated Al anode x-ray source. Surface cleanliness was verified by the absence of C and O photoelectron signals. Experimental data for the Cu $2p_{3/2}$ photoelectron line are shown in Fig. 4 for Cu and $\mathrm{Cu}_{0.5}\mathrm{Pd}_{0.5}$. It is apparent from the raw data that the alloy spectrum is broader than that of pure Cu. The $\mathrm{Cu}_{0.8}\mathrm{Pd}_{0.2}$ spectrum also showed this broadening and was almost indistinguishable from that of $\mathrm{Cu}_{0.5}\mathrm{Pd}_{0.5}$, in accord with spectral simulation using Eq. (9) for the random $A_{0.8}B_{0.2}$ lattice [7]. While the results for the $\mathrm{Cu}_{0.8}\mathrm{Pd}_{0.2}$ alloy provide important confirmation of the generality of this broadening effect, we concentrate in the remainder of the paper on a detailed analysis of the results for $\mathrm{Cu}_{0.5}\mathrm{Pd}_{0.5}$.

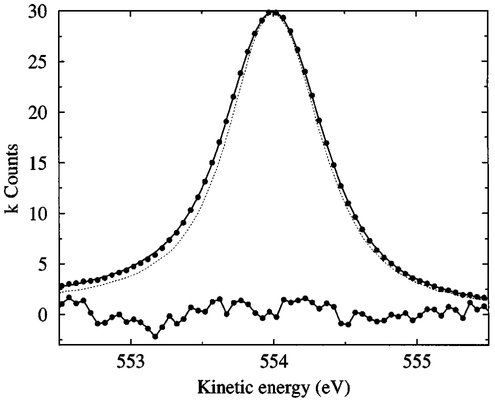

FIG. 4. Experimental Cu $2p_{3/2}$ spectrum of pure Cu (dotted curve) and $\mathrm{Cu}_{0.5}\mathrm{Pd}_{0.5}$ (circles). The spectra have been aligned in energy and placed on the same ordinate scale. Also shown is a least squares fit (solid curve) to the alloy spectrum using $W = 0.37$ eV, As described in the text, and the corresponding residuals multiplied by a factor of 10.

Following Citrin *et al.* [11] the pure Cu spectrum was least squares fitted using bulk and surface Doniach-Ŝunjić line shapes characterized by a Lorentzian width Γ and an asymmetry index α. With a surface to bulk intensity ratio of 0.12 to 1 [11] we obtained $\alpha = 0.038$, $\Gamma = 0.60$ eV, and a surface core level shift E_s of -0.25 eV in excellent agreement with Citrin *et al.* [11]. The fit also yielded $W = 0.30$ eV, in excellent agreement with the Gaussian broadening observed at the Cu Fermi edge. It is clear from a direct comparison of the raw data that a fit of the $Cu_{0.5}Pd_{0.5}$ spectrum cannot be achieved with the parameter obtained for pure Cu. Varying E_s, α, or Γ lead to poor fits (as judged by a minimum χ^2 of ~ 5) and gave strong systematic variations in the residuals. In particular, the calculated line shape was too narrow near the center of the peak while the tails decayed too slowly. However, allowing W to vary gave pleasing agreement with the experimental line shape, and we conclude that there is an additional broadening mechanism present in the alloy and that this broadening is Gaussian in character. With E_s and Γ fixed at their pure Cu values we obtained $W = 0.37$ eV and a very slight reduction in α with $\chi^2 = 1.2$. This fit is shown in Fig. 4. Increasing E_s gave rather poor results while with $E_s = 0$ we obtained $W = 0.40$ eV which we take as an upper bound. This corresponds to a maximum additional Gaussian broadening of 0.26 eV (added in quadrature) to that observed for pure Cu, and we attribute this to disorder broadening of the electrostatic potential in the alloy.

Taking λ from Wolverton and Zunger [6] Eq. (5) predicts a CCM component splitting of 0.12 eV, corresponding to a Gaussian broadening of ~0.5 eV. Thus only half of the predicted broadening is observed. Fitting the experimental data using the $Z_1 + 1$ component NNA approach confirmed this result explicitly. We attribute this to two further effects so far not considered:

(i) Short range order.—Monte Carlo simulations [6] have shown that even at high temperatures there is considerable tendency for short range ordering in the CCM point charge lattice. Since we have demonstrated that the core potential at a site is essentially determined by the nearest neighbor composition, short range order will quench disorder broadening rather effectively.

(ii) "Like-like" correlation.—The CCM neglects the direct correlation between like charges. One may expect a tendency for a charged A atom to share some of its excess charge with any neighboring neutral A atoms. This process, forbidden by the CCM, would further enhance local charge neutrality and screen out some of the disorder broadening. We may address this by noting that the dependence of elemental electronegativities on charge state can be expressed

$$\chi^i(Q^i) = \chi_0^i + \eta^i Q^i\,, \tag{11}$$

where $\chi_0^{A,B}$ and $\eta^{A,B}$ are elemental constants. Defining the ionicity of a bond between two adjacent atoms as their electronegativity difference we may suppose that the charge on a site is given by the sum of its bond ionicities. In this bond ionicity model (BIM) the Q^i and χ^i must be determined self consistently, but this generalization of the CCM retains the simplicity of intuition of basic chemical concepts.

We have shown that within the CCM the average potential for a given N_u is proportional to N_u and there is only a small amount of Gaussian scatter about these averages. Averaging out the N_u dependence we showed that $\overline{V}_{A(B)}$ the potential averaged over all $A(B)$ sites is given by $\overline{Q}/R$, corresponding to an effective Madelung constant of 1 for all structures and all compositions. Using a realistic estimate of the model parameter λ we have shown that disorder broadening of core level XPS lines in random alloys should be small but observable. XPS data for the CuPd alloy system have demonstrated the first observation of disorder broadening, but the effect was found to be significantly smaller than predicted for the perfectly random alloy. We attribute this to a tendency for a short range ordering implicit in the CCM and point out the possibility of even more efficient screening due to like-like correlation. A generalization of the CCM was presented.

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